3.3.3.9 Comparison of modelled and measured emission ratios of pure hydrocarbons

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Introduction

In order to quantify the uncertainty of emission data the individual steps by which the emission data are calculated have to be evaluated (for vehicle exhaust emissions see e.g. chapter a). For this purpose it is necessary to investigate the emissions of the individual sources in detail by determining the emission factors as well as the variability in time. In reality a huge amount of different sources contribute to the emissions of a certain region. Therefore it is reasonable to evaluate the emission data of an urban region. The modelled emission data have to be compared to results of an independent method with known uncertainties.

The quality of highly resolved emission data was thus experimentally evaluated in the joint experiment EVA. In previous chapters the measurement techniques, the design of the experiment and the methodology for data evaluation together with first results were outlined. This study focuses on a comparison between modelled and experimentally determined ratios of pure C_2-C_{10} hydrocarbons (HC_i), the sum of HC_i (:= HC_{sum}) and NO_x.

Methodology

The comparison of experimentally determined and modelled emission data requires two data sets which are comparable to each other with respect to their resolution in space, time and species. The concentration measurements downwind of the city were shown to be representative for the urban area under investigation (for a discussion see chapter b and references therein). Since a higher spatial resolution is not possible due to mixing processes and changing wind directions, the modelled data can only be evaluated based on averages over the entire urban area.

Monthly mean values of experimental data reveal the highest statistical significance due to the large number of data points and are used for analysis presented here. Another approach would be to compare daily means which reveal a high temporal resolution required for the input data of air quality models. This approach is discussed elsewhere (Mannschreck et al. 2002a).

The resolution in species of modelled and experimental data is not in any case equal. In this study only pure hydrocarbons (HC_i) i.e. compounds containing only H- and C-atoms are considered since oxygenated and halogenated HC were not quantified experimentally. On the other hand modelled emission data are in some cases given as specific compounds, in other cases as classes of unspecified compounds or solvent mixtures. The comparison therefore requires a detailed analysis of data both measured and modelled which will be explained in the following.

Measurements

The measurements of C_2-C_{10} hydrocarbons and NO_x were performed downwind of the city of Augsburg. Since measured concentrations of pollutants downwind of a source are dependent on dilution processes with background air, they cannot be used for the comparison with modelled emission data. Ratios of trace gases, however, are not influenced by dilution since both compounds underlie the same processes during transport from the source to the measurement site. In this study ratios of trace gases were calculated via regression analysis by also considering background concentration levels. Hence the given ratios are ratios of two emitted trace gases (or groups of trace gases) and do not include background levels. The measurement techniques as well as the data evaluation method are described in the previous chapter and references therein.

Hydrocarbons with a molecular weight higher than n-decane cannot be measured quantitatively since they are partly lost in the water trap of the gas-chromatographic (GC) system. Loss rates of C_{11}-C_{14} hydrocarbons were determined as 28%, 49%, 86% and >95% for undecane, dodecane, tridecane and butadecane, respectively. With the used GC-system the order of elution of a compound is according to its molecular weight. Taking into account the losses, the sum of all peak areas with a retention time higher than of n-decane is only 10% of the total peak area of C_2-C_{10} HC. Thus only a small share of total C_2-C_{14} HC is not measured quantitatively and thus not included in the experimental data.

Model

The calculation of emissions of NO_x and volatile organic compounds (VOC = oxygenated, halogenated and pure HC) is described in chapter c. The contributions of the individual source types to total VOC calculated for the Augsburg area are as follows (monthly means for October 1998 based on mass units): 74% solvent evaporation, 13% traffic exhaust, 7% fuel evaporation, 5% industrial processes, 1% residential heating.

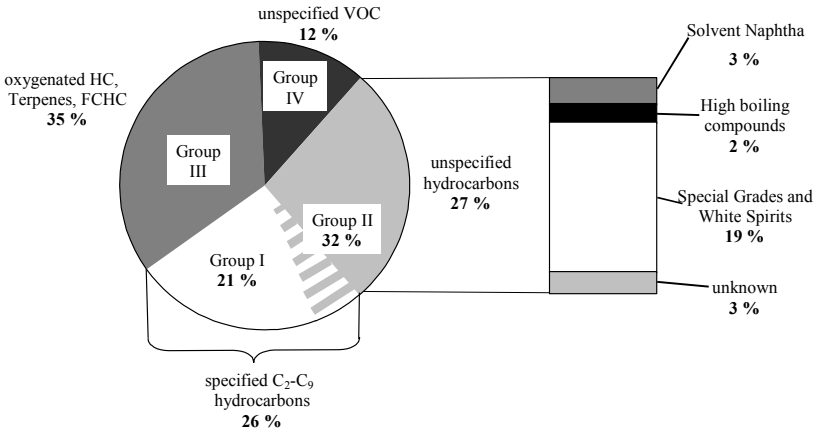

Fig. 3.31. Composition of VOC emissions for October 1998 at model default level (monthly values based on mass units).

Group I: pure hydrocarbons which 1) can be specified by the emission model as individual compounds, 2) the share in summarised compound classes (group II, see below) is smaller than 50 %, and 3) they can be measured quantitatively by the GC system. Emissions included in this group are dominated by traffic related emissions (72%) followed by solvent evaporation (12%) and other combustion processes (16%). Since all HC are specified they can be compared directly to the measured data.

Group II: pure hydrocarbons not fulfilling the criteria for group I HCs. Firstly, this group includes the specified HCs with high shares in unspecified summarised compound classes and two HCs which are not properly identified by the measurement system (striped area in Fig. 3.31). Secondly, this group contains HC which could not be further specified by the model, i.e. summarised compound classes of solvent naphtha, high boiling compounds, special grades and white spirits and hitherto unspecified HCs. Except the latter these classes are solvent mixtures which are defined according to their boiling points and consist of C_6- C_{14} hydrocarbons with different boiling limits in each of these mixtures. Although a comparison based on single compounds is not possible the share of these compounds identified and quantified by the GC-system has to be taken into account when comparing measured and modelled data.

Group III: oxygenated and halogenated HC and terpenes. These compounds were not identified in the chromatograms within this study and could therefore not be used for comparison.

Group IV: unknown VOC, no clear assignment to group I-III possible due to a lack of information on the chemical characteristics of these compounds. These emissions are mainly caused by solvents. A comparison with the measured data is not possible either.

Results and discussion

The relative contributions of specified HCs contained in group I are shown in Fig. 3.32 together with the experimental emission ratios.

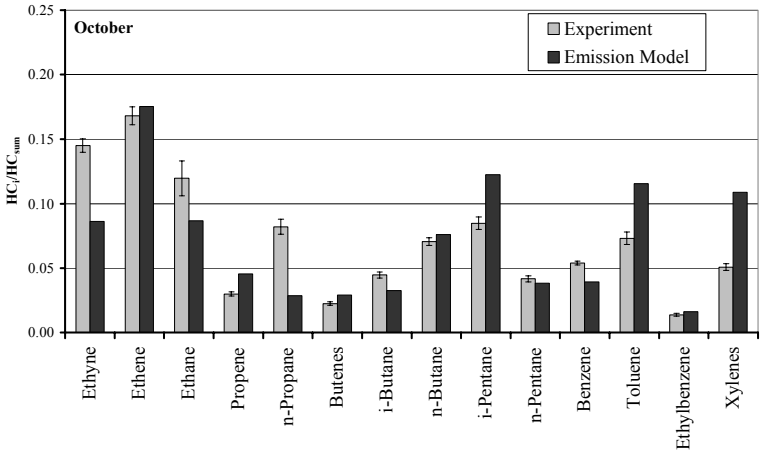

Fig. 3.32. Modelled and measured emission ratios of group I hydrocarbons (based on units of ppb). Error bars of measured data refer to the uncertainty (1 □) of the slope of the regression line.

Ethyne which predominantly originates from traffic exhaust is underestimated by the model by about a factor of two. Since ethyne is removed effectively by a properly working catalyst (Lies et al. 1998) vehicles without or with a defect catalyst and cold start emissions are important sources of ethyne (Sawyer et al. 2000). The underestimation of ethyne thus points to possibly incorrect assumptions about the share of vehicles without or with defect catalyst in the vehicle fleet and to inaccurate emission factors of cold start emissions. The emission ratio of propane is also underestimated, possibly due to incomplete emission data from individual point sources which are in some cases important propane emitters. Ratios of toluene and xylenes are overestimated by the model. According to the emission model solvent evaporation is an important source of these compounds which gives an indication of an overestimation of these emissions and will be discussed below. Also i-pentane is overestimated by the model. I-pentane emissions predicted by the model originated to a large percentage from fuel evaporation, hence the overestimation of its emissions may suggest a very high emission factor of this source or incorrect composition of fuel vapour or both. Despite these differences the agreement between modelled and experimental results is generally good.

However, for a complete comparison all modelled HC which were also measured, i.e. C_2-C_{10}-HC, have to be taken into account. Group II contains a wide range of hydrocarbons which are partly included in the measurements others are not. In order to find out the share of group II compounds identified and quantified

by the GC-system the given compound classes have to be looked at in some detail. The solvent mixtures are pure HC and are defined according to their boiling limits. Since the order of elution from the chromatographic system is according to the boiling points of the respective compounds, the approximate retention time of any HC in the chromatogram can be estimated from its boiling point. Taking into account the boiling limits of the solvent mixtures given in group II and their predicted mass percentage results in a share of 50 – 70 % of group II emissions which are detectable by the used GC-system (for more details see Mannschreck et al. (2002a)).

A comparison which takes these additional HC emissions into account cannot be based on individual compounds since these are not known. However, the parameter HC_{sum}/NO_x can be used. Absolute emission rates of NO_x were experimentally determined by two methods and compared to the modelled NO_x emission rates (chapter d and e). As a result modelled and measured emission rates were in good agreement for October. During the March campaign only one experiment was carried out and the experimental uncertainty was high so that the absolute emission rates could not be assessed. In Table 3.18 experimentally determined HC_{sum}/ NO_x ratios for October are compared first for 14 compounds of group I(HC_{sum-14}/NO_x) and secondly for all detectable compounds ($HC_{sum-all}/NO_{x)}$. In the latter case the total peak area in the C_2-C_{10} region was considered in the experimental data and the additional 50% (lower limit) of unspecified solvent emissions was considered in the modelled data. Since absolute NO_x emission rates agreed well, deviations can be attributed to HC-emission. In the case of group I HCs the two data sets agree well which was already concluded considering the HC_i/HC_{sum} ratios (Fig. 3.32). However, the modelled $HC_{sum-all}/NO_x$ ratios are substantially higher than the measured ones which can be attributed to an overestimation of group II emission.

Table 3.18. Monthly mean values of calculated and measured HC_{sum-14}/NO_x and $HC_{sum-all}/NO_x$ emission ratios for October.

Parameter [ppbC/ppb]	Model	Experiment
HC_{sum-14}/NO_x	1.9	2.0 ± 0.1
$HC_{sum-all}/NO_x$	3.9	3.2 ± 0.2

The predicted HC emissions from group II which originate mainly from solvent evaporation cannot be found in the measured data. This points to an overestimation of solvent emissions by the emission model. According to the emission model ca. 60% of all pure HC-emission originate from solvent evaporation. In the following approach the latter result can be assessed by regarding the HC-patterns, i.e. relative contribution of a HC to the total HC (HC_i/HC_{sum}). Every source type (e.g. traffic exhaust, fuel evaporation, solvents) has its characteristic HC-pattern. If the model prediction of 60% solvent emissions of pure HC was correct the measured HC pattern should exhibit large similarities or at least show the characteristic features of a solvent HC pattern. Fig. 3.33 shows the chromatograms of 5 types of grades and white spirits most frequently used in

Germany. Grades and white spirits account for approx. 65% of predicted HC-emissions from solvent evaporation and contain large shares of HC in the region of C_9-C_{12}. The relative contributions of measured HCs (dotted line) show a completely different pattern. Toluene and benzene, originating mainly from traffic exhaust, and some lighter HC have high shares whereas C_9-C_{12} HC have low or non-detectable contributions. In the case of n-decane, a compound which is exclusively emitted by solvent emissions (traffic related emissions of n-decane are below 1% (Schmitz et al. 2002)), this deviation is more than a factor of ten.

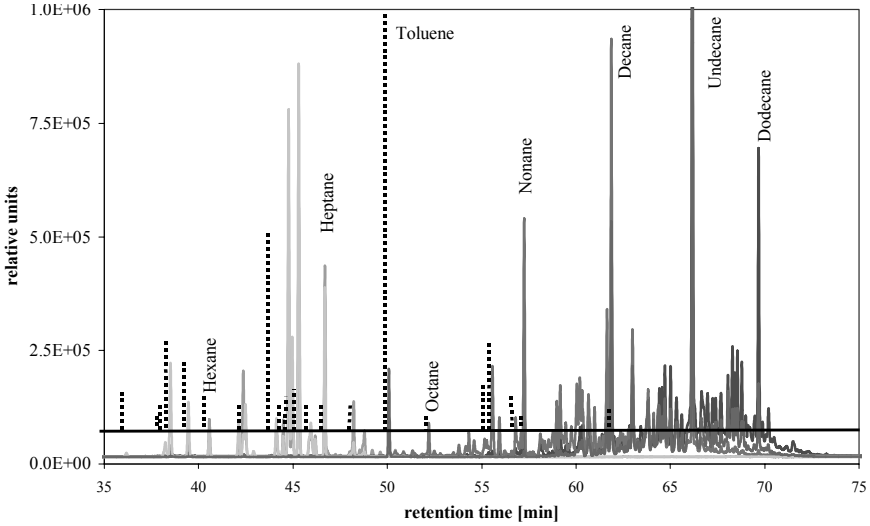

Fig. 3.33. Chromatogram of 5 grades and white spirits used most frequently in Germany and recorded with a similar GC-system as the ambient air measurements discussed here. The dotted lines show the relative contributions of HC_i to total HC measured in Augsburg and are normalised to toluene.

Conclusions

Comparisons between emission ratios (HC_i/HC_{sum} and HC_i/NO_x) derived from ground-based measurements downwind of a city and modelled emissions have been carried out to evaluate the emission model. The measurements show that urban HC-emissions are dominated by traffic related emissions. For HC which originate predominantly from traffic emissions the modelled and measured emission ratios agreed mostly within 30%.

According to the model 27% of all VOC emissions are pure hydrocarbons originating from solvent evaporation. These emissions cannot be resolved into single species but are rather given as summarised compound classes. About half of these HC-emissions are detectable by the GC system. If these additional HC-emissions are accounted for in the comparison, large deviations are found due to

an overestimation of solvent emissions. In the case of n-decane this deviation is more than a factor of ten.

A further improvement of the emission model requires more detailed investigation. Oxygenated and halogenated hydrocarbons should also be included in further experiments since they are contained in many solvent mixtures. In order to determine the apportionment of a source type to a mixture of several source types (e.g. urban emissions) the Chemical Mass Balance (CMB) method was found to be useful. The use of this method requires the knowledge of the VOC composition (VOC_i/VOC_{sum}) of all important source types in a high resolution with respect to the number of species and a known data quality. The aim of further investigations should therefore be to characterise the VOC compositions of individual source types and to close the balance for total VOC.

Summary

The agreement between the measured and calculated CO and NO_x emissions was generally better than expected on the basis of previous reports, especially on the working days. For Saturdays, however, the temporal pattern of activities contributing to emissions should be improved.

Reasonably good agreement was also observed between most of the measured and calculated NMHC/CO and NMHC/sumNMHC emission ratios for traffic related hydrocarbons. Significant differences for several substances can be attributed to specific problems, such as incorrect emission factor e.g. for ethyne. The EVA experiment revealed also significant differences between average CO/NO_x and $sumHCi/NO_x$ emission ratios measured in March and October which were unpredicted by the modelled emission ratios. This suggests that seasonal profile of activities in emission models may also need improvement.

Solvent emission seems to be the most important problem revealed by the EVA project. Modelled emission ratios of nonane and decane relative to the total measured hydrocarbons were found to be substantially higher than the measured ones. Nonane and decane are assumed to originate almost exclusively from the use of white spirits as solvents. Significant differences were also observed for compounds which are not exclusively but to a substantial degree emitted by solvents such as toluene, xylenes and higher aromatic compounds. The difference of solvent emissions obtained by measurements and by model calculations cannot presently be explained. Further studies with improved models and extensive measurements of other solvent related compounds, especially of oxygenated hydrocarbons, are needed to resolve this problem.

The EVA project presents, to the best of our knowledge, the first comprehensive evaluation of the calculated highly resolved emissions by comparison with measurements. For this purpose the technique of mass balance has been refined and the tracer technique has been used for the first time on the scale reported here. As discussed by Kalthoff et al (2002), Panitz et al (2002), and Möllmann-Coers et al. (2002a), both techniques can be further refined to reduce the uncertainties of the measured emissions. Reduction of the uncertainties in the measured emissions would result in a more stringent test of the calculated

emissions. Measurement of specific solvent compounds could also help to resolve the solvent problem.

The evaluation of calculated emissions for the city of Augsburg, though successful, still leaves at least one question open: Are the results obtained in Augsburg specific for this city or can they be generalized? This question can only be answered by further evaluations on other cities with different source composition and in other regions.

3.3.3.10 Evaluation of the Swiss emission inventory by statistical analysis of ambient air measurements from Zurich and Wallisellen

Johannes Staehelin

Introduction

The planning of the most cost effective strategy to reduce air pollution and greenhouse gases is based on inventories of anthropogenic emissions. The reliability of such emission inventories is therefore very important for any appropriate political action in this field. However, the evaluation of emission inventories, which are usually based on emission models of varying degree of sophistication by an independent method is not a simple task. Measurements of road tunnels can be used for comparison with road traffic emission models (see Staehelin and Sturm 3.3.2.1.). Another approach is the statistical analysis of ambient air measurements of primary air pollutants. Chemical Mass Balance models (CMB) have been often used for this purpose. Such studies are particularly valuable, if the respective emission sources emit simultaneously a large number of compounds and if the relative composition of the dominant sources is characteristically different. They are based on the following matrix equation:

$$\boldsymbol{X} = \boldsymbol{S} * \boldsymbol{Q} + \boldsymbol{\varepsilon} \qquad \textbf{(3.11)}$$

Matrix of ambient air concentrations	=	Activities of sources	*	Source Profiles	+	error term
measured		*to be determined*		*prescribed*		*to be minimized*

In CMB models the observed measurements are interpreted as a superposition of emission sources with constant relative composition (source profiles (Q)). The fit of the measured air pollutant concentrations (X) allows the determination of the contributions of the sources to the ambient air quality (activities of the sources (S)). However, CMB-models require the knowledge of the composition of all relevant emission sources, which is often not adequately known. In the presented study we show another recently developed method which does not require the knowledge of the source profiles (Staehelin et al. 2001). The method is based on